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Impact on Recovery of Pulping and Bleaching Changes to Meet the EPA Cluster Rule

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IMPACT ON RECOVERY OF PULPING AND BLEACHING CHANGES TO MEET THE EPA CLUSTER RULE

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ABSTRACT

Pulping and bleaching practices have changed over the past several years due to concern about the impact of mill effluent on the environment. The proposed EPA Cluster Rule sets even tighter limits on bleach plant and mill effluent which will cause further changes in pulping and bleaching practices. All of these changes will have direct impact on the operation of the recovery department. Bigger impacts on recovery can be expected if bleach plant effluent is recycled back to pulping in an effort to "close" the mill cycle.

The purpose of this paper is to estimate the impact of various pulping and bleaching changes on the recovery department. The character of black liquor from a conventional pulping process is first examined. Changes in pulping parameters such as AA-to-wood ratio and H-factor are shown to have substantial effect on the yield/kappa number relationship, but a rather smaller effect on recovery. This will be followed by estimates of the impact on recovery of various modifications such as the use of high sulfidities, anthraquinone, and oxygen delignification. All of these are shown to impact the heating value and load on recovery by less than 5%. Bleach plant filtrate recycle brings both organic and chloride into recovery. Chloride is the most important non-process element in recovery. The impact of proposed pulping and bleaching changes on its concentration in black liquor is estimated.

INTRODUCTION

Recently the US Environmental Protection Agency proposed new regulations for the effluent and non-combustion-source air emissions from pulp and paper mills (1). These regulations are collectively referred to as the Cluster Rule. They extend previous effluent regulations to include new pollutant categories such as Absorbable Organic Halides (AOX), Chemical Oxygen Demand (COD), effluent color, and a suite of chlorinated organic compounds which can occur in bleach plant discharges. The conventional pollutants, Biological Oxygen Demand (BOD) and Suspended Solids (SS) are also covered by the Cluster Rule. The specific limits on these pollutants will not be finalized until the Cluster Rule is promulgated into law. Whatever the final limits are, they will be strict enough to ensure that changes in every aspect of mill operation will be required to reach compliance. Many of the changes will affect the recovery operation. It is the purpose of this paper to examine the impact of some of these changes on recovery operations.

The pollutant species regulated by the proposed Cluster Rule are all organic materials, AOX, color, COD, BOD, SS and chlorinated organics. Much of the compliance strategy involves routing more organic material through the recovery system for destruction in the recovery boiler rather than allowing them to be discharged with the mill effluent. In mills producing unbleached products, organic material reaches the effluent by means of black liquor spills, open screening operations, wet debarking, and discharges of white water from the pulp or board machine. In addition to these sources, mills producing bleached products also have the discharges from the bleach plant. Bleach plant discharges are a very major portion of organic material in mill effluent, and, for bleaching operations which are not Totally Chlorine Free (TCF), they are the only source of AOX.

It is useful to estimate the additional organic load on the recovery system if all the organic material not found in the pulp were to pass through recovery for destruction. Current pulping practice results in brownstock pulp with a yield of about 47% and a kappa number for softwood of about 30. This kappa number corresponds to a lignin content of about 4.5% on OD pulp, or about 21.1 kg per tonne of OD wood. The organic separated from the wood becomes the organic in black liquor. This is about 530 kg per tonne of OD wood. Comparing these two figures indicates that the additional load on the recovery boiler due to the need to destroy additional organic represents an incremental organic load of about 4%.

The first section of this paper presents the various means of diverting additional organic from the effluent to the recovery operation at various stages of the pulping and bleaching processes. The second section presents a set of simple models for pulping, bleaching, and black liquor heating value which can be used to estimate the impact on recovery operations of various process changes. The final section presents some model results for these impacts.

PULPING AND BLEACHING CHANGES TO REDUCE ORGANIC DISCHARGES

The purpose of Kraft pulping and bleaching is to separate the fiber in the wood (or other feedstock) from the lignin which holds the fibers together. Kraft pulping typically removes about 90% of the lignin, but also removes 50% of the hemicellulose and 20% of the cellulose. Most of this dissolved material ends up in the black liquor.

In the early bleaching stages, the process of lignin removal continues. The later bleaching stages modify the remaining lignin in the pulp to brighten the final product. Bleaching is much more specific in removing lignin and leaving the cellulose and hemicellulose than pulping. Because chlorine compounds have traditionally been used as bleaching agents, the organic materials removed during bleaching have not been routed through the recovery operation, but rather have been discharged from the mill.

Many of the schemes for reducing organic discharges from the mill involve recycling bleach plant filtrates back into the pulping and recovery departments. Many schemes retain chlorine compounds as bleaching agents, but significantly reduce the quantity of chlorine used by reducing the lignin content of the pulp entering the bleaching department. Bleach filtrate recycle may also be accomplished through the use of alternative bleaching agents such as oxygen, peroxide, and ozone which are more compatible with recovery.

Pulping Modifications

Conventional Kraft pulping can be carried out to remove a larger portion of the lignin, but this has the very negative economic impact of reducing the yield of pulp. All the modifications to conventional pulping attempt to reduce residual lignin in the pulp while avoiding or reducing yield loss. The three methods for doing this are: 1) adding chemicals such as anthraquinone (AQ) to the cook, 2) modifying the time-temperature profile or the time-chemical charge profile during the cook or, 3) adding a stage after cooking for delignification by reaction with oxygen.

The impact on the pulp yield and residual lignin for two of these, AQ and oxygen delignification, will be discussed below in the model presentation section. The third method is generally referred to as extended or modified cooking. There are equipment and procedures to take advantage of the improvements from this type of pulping available from each vendor of both batch and continuous digesters. The overall impact of these cooking techniques will be similar to that of conventional cooking followed by oxygen delignification. Because this latter combination has been more thoroughly characterized, it will be investigated below for its impact on recovery.

All pulping and delignification stages are followed by washing stages. Pulp washing separates the organic that has been dissolved during pulping or delignification from the pulp. The final filtrate from these washing operations is the weak black liquor.

Pulp washing is not perfectly efficient at removing black liquor solids from the brownstock pulp. A small residual content of black liquor enters the bleach plant and is mostly removed there. In a mill producing unbleached products, this black liquor may find its way into the paper machine white water. The washing efficiency is often characterized by the sodium or equivalent saltcake (Na_2SO_4) lost with the washed brownstock pulp. This ranges from about 3 to 45 kg saltcake per tonne of pulp. These losses correspond to overall washing efficiency between 95.5% and 99.5%. Considering the estimate in the Introduction of 4% for the potential increase in total organics to recovery, it is clear that changes in washing efficiency of brownstock may be as significant as some of the other changes in pulping operations.

Bleaching Modifications

Pulp bleaching has gone through very rapid change in the past decade and this is certain to continue in the immediate future. The two principle chemicals used in conventional pulp bleaching are chlorine gas (Cl_2) and chlorine dioxide (ClO_2). Traditionally, Cl_2 has been used in the first stage of bleaching primarily for removal of lignin from the pulp. ClO_2 has been used in the later bleaching stages to chemically modify the remaining lignin in the pulp in order to brighten the final product. Using "C" to represent a Cl_2 stage, and "D" to represent a ClO_2 stage, and "E" to represent a caustic extraction stage used to remove dissolved lignin, a very conventional 5-stage bleaching sequence would be CEDED.

Many bleaching schemes have been proposed to replace conventional bleaching sequences. All of these schemes seek to eliminate elemental chlorine (Cl_2). Some schemes seek to eliminate all chlorine. The former is referred to as Elemental Chlorine Free (ECF), while the latter is Totally Chlorine Free (TCF).

Replacing some or all of the Cl_2 in the first bleaching stage with ClO_2 is called "substitution". Because ClO_2 has greater bleaching power than Cl_2 and contains less chlorine, substitution has a dramatic effect on both the total chloride in bleach plant filtrate and on the formation of chlorinated organic compounds. ClO_2 substitution also has impacts on the main function of the bleach plant, delignification and brightening, which are major considerations in its use. Only the aspects of substitution which might directly affect the recovery department will be addressed here. The chloride content of any bleach plant filtrate recycled to recovery would be the most significant impact.

Other bleaching schemes which use chemicals such as oxygen, peroxide, and ozone will not be directly addressed below. The relative magnitude of their impact will be similar to recycling bleach filtrates from ClO_2 bleaching, with the exception of the impact of chloride. The residual lignin content of the pulp entering the bleaching department determines the organic that can be removed during bleaching. The bleaching chemicals and sequence determines how degraded the organic material is, and the content of inorganic accompanying it. In general, chlorine bleaching degrades the lignin less than the oxygen-based compounds, so it represents a larger impact on recovery heat load and, of course, chloride load.

MODEL DESCRIPTION

Black Liquor Heating Value

The black liquor heating value model used here is a very modestly modified version of a robust model proposed by Green and Grace (2). Several models of black liquor heating value are available in the literature (3-4). These models all differ slightly in complexity and specific results. What was sought for the present application was a model which would correctly portray the levels and trends in the black liquor heating value for changes in pulp yield, residual lignin, pulping conditions, and pulp washing efficiency.

The Green and Grace(2) method has been modified here in four ways. The first modification involves the use of a pulping model (discussed below) to relate pulping conditions to pulping results. In the original model, the active alkali-to-wood ratio in the digester could be specified separately from the pulping yield. These two parameters are the most important in determining both the inorganic and the organic content of the black liquor. In practice, they are not independent. The AA-to-wood ratio has a major impact on pulp yield, as will be shown below.

The second modification involves the combination of two classes of black liquor organics into one class. The Green and Grace method recognizes 1) resins and fatty acids (RFA), 2) volatiles, 3) lignin (which is different for hardwood and softwood), 4) organic acids from carbohydrates (OAC), and 5) miscellaneous organic compounds (MOC). Each class of organic material has an assigned heating value. In the current use of the model, the RFA volatiles and lignin remain the same, but the OAC and MOC are combined into a category called "carbohydrates" and are given the heating value of the OAC. This change has very little impact on the calculated results. It does remove a category, MOC, which would be difficult to characterize for most woods. This change results in a breakdown of the components of wood into four categories: volatiles, extractives, lignin, and everything else. The breakdown of the components of wood and their assumed heating values are shown in TABLE 1.

TABLE 1 - Components of Wood Found in Black Liquor

	Hard-wood	Soft-wood	Hardwood MJ/kg (Btu/lb)	Softwood MJ/kg (Btu/lb)
Volatiles	1%	1%		
Extract-ives	3%	3%	37.72 (16,224)	37.72 (16,224)
Lignin	22%	27%	25.12 (10,805)	26.92 (11,578)
"Carbo-hydrates"	by diff.	by diff.	13.56 (5,832)	13.56 (5,832)
Cellulose				

The "carbohydrates" content of black liquor is calculated in a manner similar to the Green and Grace method. The fraction of carbohydrates is 100% less the volatiles, extractives, yield, and the difference between the lignin in the wood and the lignin in the pulp. This breakdown of wood into four categories makes calculation of the hydrogen content of the organic easier, which is useful for the calculation of the Net Heating Value (NHV). The Higher Heating Value (HHV) includes an energy term due to oxidation of reduced sulfur in the black liquor, and a term for condensation of water formed from hydrogen in the black liquor during combustion. Neither of these terms is available during combustion of black liquor in a recovery boiler. The NHV is, therefore, a better measure of the actual heat load on the boiler. The hydrogen content assumed for each component of the black liquor is given in TABLE II.

TABLE II - Hydrogen Content of Wood Components

Component	Hydrogen
Extractives	12%
Lignin	6%
"Carbohydrates"	6.5%

The final modification to the original Green and Grace method is in the calculation of the white liquor density and percent solids. Here, these two are calculated from the specified Total Titratable Alkali (TTA), Active Alkali (AA), and sulfidity.

Pulping Model

The pulping model used here is one reported in a thesis by Spencer (6). The same model is reported incorrectly in reference (7). The values for all the coefficients used in the present work are given in the appendix to this paper. This model is based on multiple linear regression of the results of 115 pulping experiments. These experiments used southern yellow pine chips in laboratory batch pulping experiments covering the range of the parameters shown in TABLE III.

This model has the advantages of algebraic correlations, which include all the important pulping variables, as well as the effects of anthraquinone on pulping results. The trends predicted by this model compare favorably to those reported for other models (8,9,10) though exact comparison is not possible due to differences in wood species used as the basis for the model development. The specific results of the present work are restricted to batch digestion and southern yellow pine, though the general levels and trends reported here probably apply more widely.

TABLE III- Parameter Range in Experiments Used as the Basis of the Pulping Model (6)

Parameter	Range
AQ	0-0.5% on wood
Effective alkali	14-23%
Sulfidity	11-55%
Liquor to wood ratio	2.4-6.8
Temperature	157-187°C(315-369°F)
H-factor	1100-3700

The pulping model predicts five results for any given set of pulping conditions: 1) the total yield, 2) the screened yield, 3) the pulp kappa number, 4) the unbleached pulp viscosity and, 5) the residual effective alkali. Only the total yield and the kappa number are used in the present work. The actual yield of pulp going to the bleach plant is the screened yield. However, for the range of conditions used here, the screened yield and the total yield are almost identical.

The kappa number is a measure of the amount of lignin that remains in the pulp after pulping and washing. The relationship between kappa number and residual lignin is:

*Residual lignin = kappa number*0.15% on OD pulp* (1)

This means that for a conventional cook of a softwood to a kappa number of 30, the residual lignin in the pulp is 4.5% or 45 kg lignin/tonne pulp. For a hardwood cook, the typical kappa number is 20, making the residual lignin 30 kg/tonne. In both cases, the yield would be between 44% and 49% of the dry wood.

Yield and kappa number are the two key parameters in pulping as far as recovery and bleaching operations are concerned. The pulp quality, as measured by other properties such as pulp viscosity, is of major concern to the overall economic viability of the mill. Yield, however, is the key parameter determining the quality of organic matter in the black liquor, and kappa number determines the amount of lignin that must be removed or brightened in the bleach plant. A plot of yield versus kappa number of the pulp gives an easy comparison of the impact of different pulping variables, and the impact of some alternative schemes. The pulping model was used to generate the graphs in Figure 1. Shown in this figure is the yield/kappa number relationship obtained by varying one of the four variables at a time: sulfidity, H-factor, AA-to-wood, and AQ. The central value and the variable ranges are given in TABLE IV.

TABLE IV - Central Value and Range for the Four Pulping Variables in Figure 1.

Parameter	Low	Central	High
AQ	0%	0%	0.2%
AA/wood	12%	18%	24%
Sulfidity	20%	30%	40%
H-factor	800	1800	2400

The H-factor is a pulping variable which gives an integrated value of the time-temperature profile during cooking which reflects the kinetics of the pulping reactions.

Figure 1 shows the typical trade-off of yield and kappa number for sulfidity, H-factor, AQ, and AA-to-wood. The kappa number of the pulp leaving the pulping department can be lowered, but at the expense of the pulp yield. These plots are for a softwood (southern yellow pine) so the typical result might be something like the central values shown here, a yield of 47% for a kappa number of 30. For the AA-to-wood and H-factor curves, the yield drops to about 44% when a kappa number target of 20 is used. Only 1.5% additional lignin is removed, but the yield dropped by 3%. The curve for varying sulfidity is considerably flatter, and therefore better, than for the other two pulping variables, but very high sulfidities (above 35%) are required to obtain these results. The results with AQ are even better, but the cost and diminishing returns on the use of AQ have, so far, limited its use in North America. When reviewing these results, keep in mind that the pulping experiments can be run at the conditions stated, and the yield and kappa number will be as shown, but not all of these conditions would produce high quality pulp, either for bleaching or ultimately for sale as a product.

O_2 Delignification Model

The chemical reactions in conventional pulping are not very lignin-specific. Continued pulping to lower kappa number with conventional pulping does not produce a quality product. One alternative is to continue delignification by reacting the washed pulp with oxygen in a separate stage. This process of oxygen delignification is well established technology (11). Within the range of normal practice, oxygen is very specific to lignin removal in either of two basic configurations: medium consistency or high consistence. Delignification by 50% can be achieved with little loss in pulp yield other than lignin loss. The reaction is carried out under alkaline condition using either caustic or oxidized white liquor. For the present work, oxidized white liquor is assumed. It was further assumed that 0.12% of both oxygen and caustic are consumed for each point reduction in pulp kappa number (11,12). The mass and species balance around the oxygen delignification process would be quite simple if it were not for the fact that oxygen reacts with lignin and reduces its heating value.

In the oxygen delignification model used here, the percent reduction in pulp kappa number is specified, so the caustic and oxygen consumption is known (0.12%*kappa number) and the lignin removed is also known (from the definition of kappa number, lignin = 0.15%*kappa number). The chemical oxygen demand (in combustion parlance, the stoichiometric oxygen-to-fuel ratio) is close to 1.5 kg O_2 per kg of lignin. This means that kappa number*0.15%*1.5 or kappa number*0.225% of oxygen would be required to completely oxidize the lignin removed during oxygen delignification. The value 0.12%*kappa number of oxygen supplied represents about 53% of the total COD. The heating value of the organic removed during oxygen delignification has been reduced in the model by this amount from the initial lignin heating value shown above in TABLE I. This allows both the quantity of material removed during O_2 delignification and the total heating value of this material to be calculated though the organic/inorganic composition is not well known.

Figure 2 shows the result of using oxygen delignification on the pulp produced from the central point conditions shown in TABLE IV and Figure 1. For reference, the plot obtained with varying AA-to-wood ratio is also shown. Oxygen delignification produces a much flatter, and therefore better, trade-off of yield and kappa number than the harsher conditions of increased AA-to-wood. In addition, practical experience shows that delignification by 50% is currently possible with very modest impact on pulp quality. Many schemes to take advantage of this technology have been put forward (11,13).

Figure 1—Impact of pulping variables on the yield and kappa number relationship.

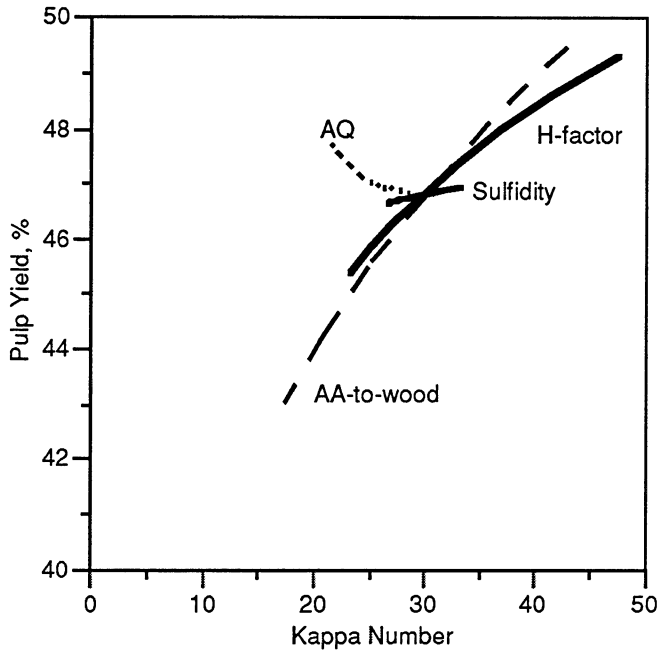
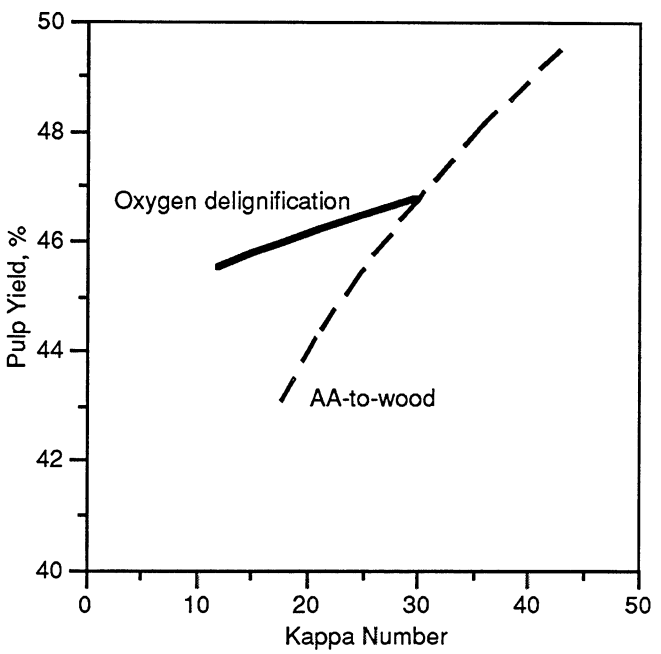


Figure 2—Impact of oxygen delignification on the yield and kappa number relationship.



Bleaching Model

Because the emphasis of the present work is on the impact on recovery operations rather than pulp quality, a very simple bleaching model is adequate. This model assumes that bleach plant filtrate recycle to recovery would consist of all remaining lignin in the pulp after post-oxygen washing, all chlorine added in the first bleaching stage, and all caustic used in the first extraction stage. This model ignores all chlorine compounds added to the later bleaching stages, and any additional caustic in later extraction stages. It does, however, account for all organic material that could be dissolved during bleaching.

The amount of chemical applied to the first bleaching stage is usually specified in terms of the Kappa Factor (KF) or Active Chlorine Multiple. This is the amount of equivalent chlorine applied per unit of kappa number in the unbleached pulp. A typical value of the kappa factor would be 0.2% on pulp. This kappa factor means that for a pulp kappa number of 30, about 6% Cl_2 on pulp or 60 kg Cl_2 per tonne of pulp would be charged in the first stage. About 10% of this would form AOX in the bleach plant discharge, or 6 kg/tonne pulp (14). This is quite a high value compared to the proposed Cluster Rule limit for AOX of 0.156 kg/tonne in the effluent. Clearly much lower unbleached kappa numbers and kappa factors would be needed to reduce AOX to the proposed levels.

Fortunately, chlorine dioxide has proven to be a good substitute for chlorine. The equivalent bleaching power of ClO_2 is 2.63 times that of Cl_2, and the chlorine in ClO_2 is only 52.6%. This means that the same bleaching potential can be obtained from ClO_2 with only 20% of the atomic chlorine. The percent ClO_2 substitution is based on equivalent bleaching power so:

$$Equivalent\ chlorine = (kappa\ number)*(kappa\ factor) \quad (2)$$

$$Equivalent\ chlorine = Cl_2 + 2.63*ClO_2 \quad (3)$$

$$Substitution = \frac{2.63*ClO_2}{Cl_2 + 2.63*ClO_2} \quad (4)$$

The atomic chlorine in the bleach plant discharge from the first stage is:

$$Atomic\ chlorine = Cl_2 + 0.526*ClO_2 \quad (5)$$

where both Cl_2 and ClO_2 are in kg per tonne of pulp.

MODEL RESULTS

The models of pulping, O_2 delignification, bleaching, and black liquor heating value have been combined and exercised over a range of conditions. The purpose of this effort is to assess the impact on recovery operations of conventional pulping, pulping modifications, and bleach plant filtrate recycle.

Figure 3 shows the impact of white liquor sulfidity on total black liquor solids to recovery. It also shows the HHV and NHV of the black liquor for conventional pulping condition without O_2 delignification or bleach plant filtrate recycle. Higher sulfidity increases both the black liquor solids to the boiler per tonne of pulp and the HHV. However, the NHV is nearly unaffected by the sulfidity level. From the midpoint value of

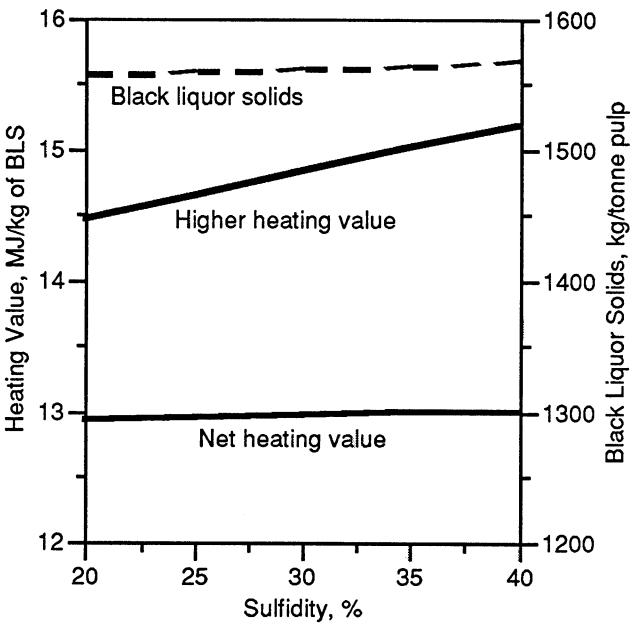


Figure 3—Impact of sulfidity on black liquor heating value and solids to recovery.

30% sulfidity, the flow of black liquor solids changes by only ± 0.3 %, the HHV by ±2.4%, and the NHV by only ± 0.2 %. This result is not surprising considering the pulping results shown in Figure 1. The change in pulp yield with increased sulfidity is less than the loss of lignin from the brownstock pulp. For the range of sulfidities from 20% to 40%, the predicted kappa number decreases from 33 to 27, a drop of 0.9% in residual lignin. For the same range, the yield decreases by only 0.4%, indicating that more cellulose remains in the pulp at higher sulfidities.

The change in black liquor solids per tonne of pulp along with HHV and NHV is shown in Figure 4 as a function of AA-to-wood ratio. Here, both the HHV and NHV decrease while the black liquor solids per tonne of pulp increases, all due to the increased inorganic load at higher AA-to-wood ratios. The actual heat load on the boiler is the product of the black liquor solids per tonne times the NHV. This increases by 13% as AA-to-wood is increased from 15% to 20%, mostly due to a predicted decrease in yield from 48.2% to 45%. This increase is also partly due to a decrease in pulp kappa number from 34.9 to 22.3. Both decreased yield and decreased kappa number send more organics to recovery.

Figure 5 shows the impact of anthraquinone used in pulping on recovery operation. The HHV and NHV of the black liquor are almost unchanged, but the BL solids per tonne decreases by 2.5%. Figure 1 shows the reasons for this. With AQ addition, the yield goes up while the kappa number goes down. This means that less cellulose and hemicellulose are removed while more lignin is removed. The net quantity of organic material in the black liquor is less, but the carbohydrates with lower heating values are replaced with lignin fragments with greater heating value. The overall result is very little impact on HHV and NHV. The total heat load on the recovery boiler decreases by 1.7% with addition 0.2% AQ on wood according to the model.

Figure 6 shows the impact of adding an O_2 delignification stage after conventional pulping to a 30 kappa number. Figure 6 also gives an

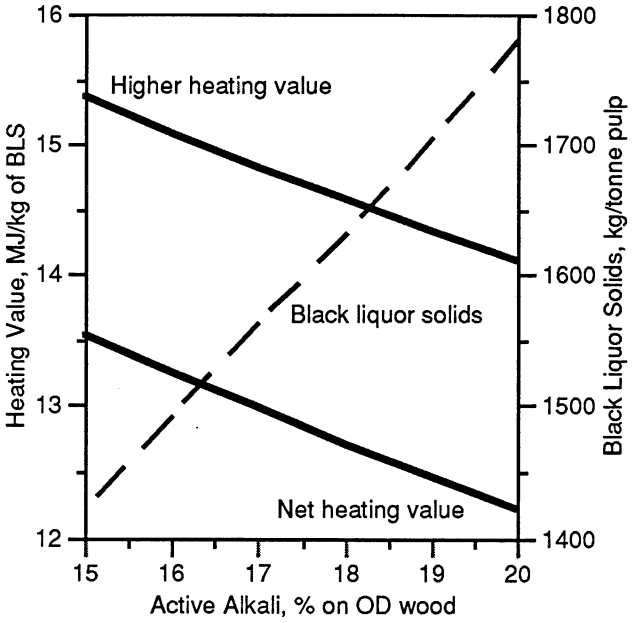


Figure 4—Impact of active alkali charge on black liquor heating value and solids to recovery.

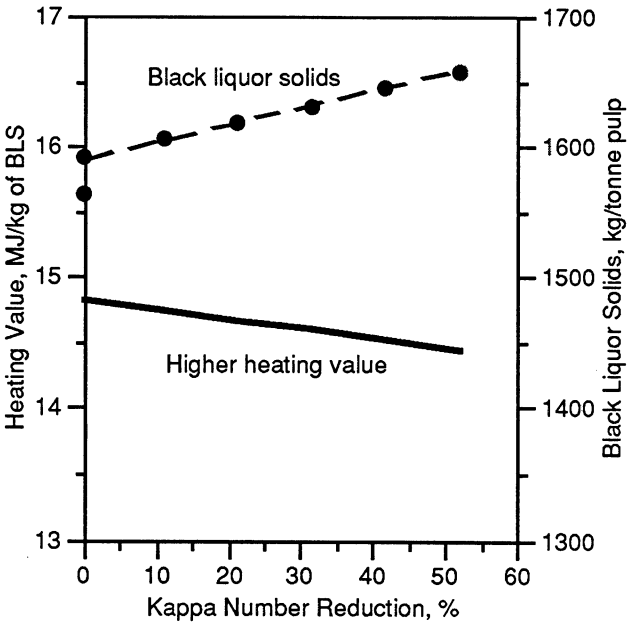


Figure 6—Impact of oxygen delignification on black liquor heating value and solids to recovery.

indication of the impact of pulp washing changes. The first two points on the black liquor solids curve at 0% kappa number reduction with O_2 delignification are for two different levels of washing. The lower point is for washing to a saltcake loss of 20 kg/tonne of unbleached pulp. The upper one is for 2 kg saltcake loss per tonne of unbleached pulp. This change would be due solely to adding an additional washing stage after normal brownstock washing. The remaining part of this curve shows changes due to oxygen delignification. More inorganic and organic material goes into the black liquor. However, because the organic is partially oxidized during O_2 delignification, the heating value of the additional organic is low. Looking only at the O_2 stage, the increase in black liquor solids is 4%, while the combined black liquor heating value decreases by 2.6%. Note that for the washing conditions selected, the change in solids due to washing is 1.8%, almost the same magnitude as O_2 delignification.

Figure 5—Impact of anthraquinone on black liquor heating value and solids to recovery.

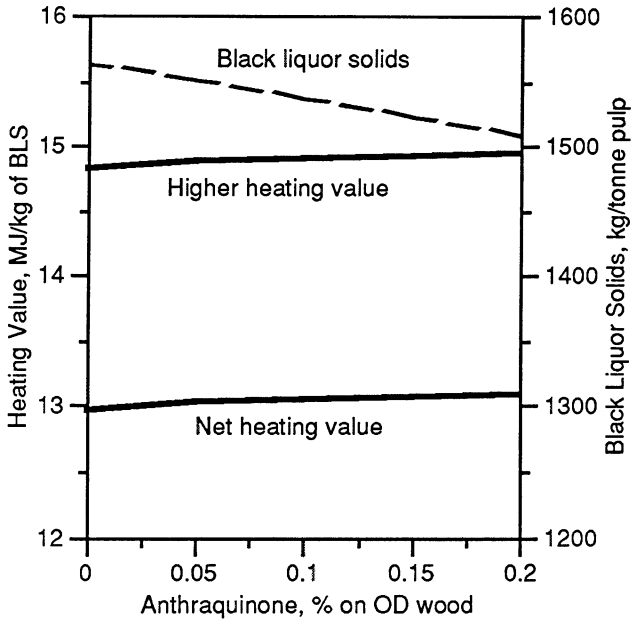


Figure 7 shows one aspect of recycling bleach plant filtrate to the recovery department. This effect would be the same whether the recycle of filtrate were by means of countercurrent brownstock washing or direct recycle of concentrated bleach filtrate to weak black liquor. Recycling would bring organics, inorganics, and particularly chlorine into the black liquor. Starting with a conventional cook to kappa number 30, followed by O_2 delignification to kappa number of 15, the additional heat load brought back to recovery by bleach plant recycle would be about 2.8%. The increased black liquor solids per tonne would be about 4.4%. Figure 7 addresses the issue of increased chloride level in the black liquor. Decreased kappa factor and increased ClO_2 substitution both help reduce this load, but it is still very high. For the incoming kappa number of 15, a kappa factor of 0.2%, and 100% substitution, about 6 kg Cl/tonne is brought into recovery.

Purging some of the increased chloride load with recovery boiler precipitator dust is possible. However, assuming the typical conditions listed in TABLE V for the recovery boiler, only about 2.5 kg Cl/tonne could be purged in this way. Comparing this to the potential input of Cl from bleach filtrate recycle shows that lower inlet kappa numbers and lower kappa factors would be required to make the Cl input small enough to be purged with precipitator dust.

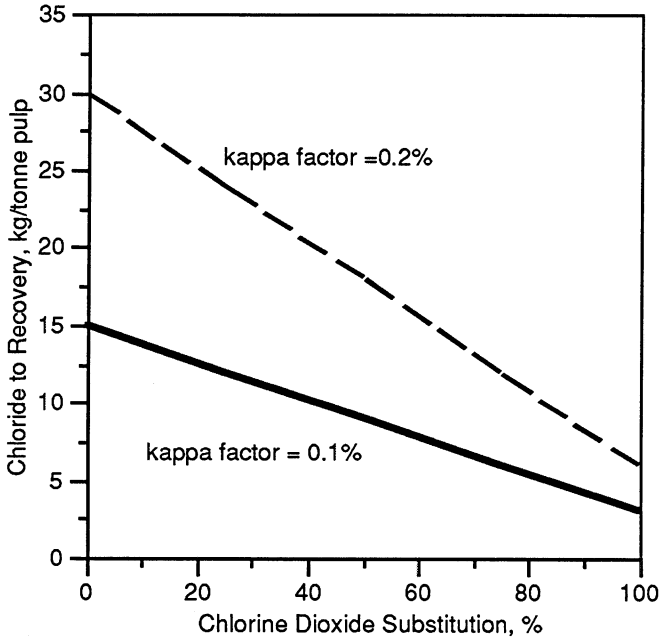


Figure 7—Impact of ClO_2 substitution on chloride to recovery with bleach plant filtrate recycle.

TABLE V - Parameters in Calculation of Cl Removal from Precipitator Dust.

PARAMETER	TYPICAL	RANGE
Black liquor solids	1600 kg/odt pulp	1400-1800
Sodium in BLS	19%	18-20
Na volatilized to fume/dust in RB	10% of Na in BLS	8-12
Total Na makeup to mill	10 kg/odt pulp	5-20
Cl/Na in BLS	3%	1-35
HCl loss	5% of Cl in BLS	0-25
Cl in BLS	0.6% of BLS	0.2-7
Cl/Na enrichment in fume/dust	2.5 x Cl/Na in BLS	2-3

CONCLUSIONS

Models for pulping, oxygen delignification, bleaching, and black liquor heating value, have been brought together to investigate the impact on recovery of various operating strategies. The main focus of the work is on those operating strategies adopted to reduce the discharge of organic materials with the mill effluent. Two of the models used, pulping and black liquor heating value, were taken from the literature with only minor modification. The other two models are fairly simple material and species balances. All the models were selected or developed specifically to address issues of recovery impact, so they have limited value in assessing other aspects of modified operating strategies.

The overall conclusion from this work is that the changes in both heating value and black liquor solids flow per tonne of pulp are relatively modest for the strategies investigated. The strategies were conventional pulping changes, oxygen delignification (with changes in pulp washing efficiency), and bleach plant filtrate recycle. The impact on recovery of any single change is less than 5%. This is in the range of incremental recovery capacity. Where this is definitely not the case is the increase in chloride input with recycle of the filtrate from the first two stages of bleaching. Recycle of this material could increase chloride input to recovery by a factor of 8, even with a kappa number of 15 entering bleaching, and 100% substitution of ClO_2 for Cl_2.

REFERENCES

1. Environmental Protection Agency, 40 CFR parts 63 and 430, Effluent Limitations Guidelines, proposed rule, Federal Register 58 (241), Dec. 17, 1993.
2. Green, R. P. and Grace, T. M., "A method for calculating the composition and heating value of black liquors from kraft and polysulfide pulping," Tappi J., 67 (6): 94 (June 1984).
3. Annergren, G. E., Haglund, A., and Rydholm, S. A., "On the composition and fuel value of black liquor," Svensk Papperstid, 71: 497 (1968).
4. Gullichsen, J., "Heat values of pulping spent liquors," Sym. on Rec. of Pulping Chems., IUPAC-EUCEPA, Helsinki, Finland: 211 (1968).
5. McDonald, K. L., "Calorific value of spent liquors by carbon analysis," Tappi J., 60 (12): 107 (1977).
6. Spencer, Ph.D. thesis, IPC, Appleton, WI, (1982).
7. "Alkaline Pulping," Pulp and Paper Manufacture, Vol. 5, M. J. Kocurek editor, TPAAI/CPPA Joint Textbook Committee of the Paper Industry: 71 (1989).
8. Hatton, J. V., "Development of Yield Prediction Equations in kraft pulping," Tappi J., 56 (7): 97 (1973).
9. Tasman, J. E., in ref. 7 above., p 71.
10. Agarwal, N. and Gustafson, R., "On the modelling of kraft pulping," TAPPI Pulping Conf., 1073 (1993).
11. TAPPI Intl. Oxygen Delignification Conf., San Diego, CA, (June 1987).
12. McDonough, T. J., "Oxygen Delignification," TAPPI Bleach Plant Operations Shortcourse, (1992).
13. Samuelson, O. and Ojteg, U., "NO2 treatment of pulp followed by oxygen bleaching," Tappi J., 73 (2): 141 (1990).
14. McDonough, T. J. and Courchene, C. E., "Regression models to predict levels of AOX generation," IPST, (June 1993).

APPENDIX
PULPING EQUATIONS USED IN MODEL(6)

Pulping Variables	Typical Values
AQ = anthraquinone, % on od wood	0.1%
TEMP = temperature, °C	170°C
EA = effective alkali, %	15%
SULF = sulfidity, %	30%
LW = liquor-to-wood ratio	4
HF = H-factor	1800
Dummy variables	**Typical Values**
A = AQ	0.1
As = SQRT(AQ)	0.316
T = TEMP/1000	0.17
E = EA/100	0.15
S = SULF/100	0.3
L = LW/10	0.4
H = HF/10000	0.18

Pulping Equations

$$Log(total\ yield) = \sum_i a_i * x_i$$

$$Log(kappa\ number) = \sum_i b_i * x_i$$

Equation Constants

x_i	a_i	b_i
constant	1.561	1.12
A	0.0502	
As	0.3529	0.273
T	2.02	7.481
E	0.773	–4.572
S	–0.133	–1.348
L	–0.434	2.282
H	0.141	0.2182
As*T	–1.812	–6.588
As*L	–0.136	
T*E	–10.87	
T*L	2.085	
T*H	–3.758	–20.23
E*L	1.046	
S*H	0.3111	
As*E		1.773
As*S		0.9294
As*L		–0.6266
As*H		1.169
S*S		1.059
S*L		–1.578
S*H		2.134
L*H		–4.241
H*H	0.4479	5.574